Oxidation of Laser Ablated Uranium Nanoparticles

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A significant contribution to Condensed Matter Research : Understanding the behavior of 5f electronic systems

To obtain a detailed predictive description of the structural and electronic properties of actinides materials

<u>Scientific Goal</u>

Experimental benchmark of the theory

e. g. Bandmapping

↓ yields

Confirmed theoretical description of the structural and electronic properties of α and δ Pu

↓ affords

<u>Programmatic Goal</u>

Predict Behavior of Pu over 10's of years.

e.g. Vacancy mobilities and dislocation mobilities

Photoemission and bandmapping as a function of size on the nanometer-scale affords separation of correlation effects

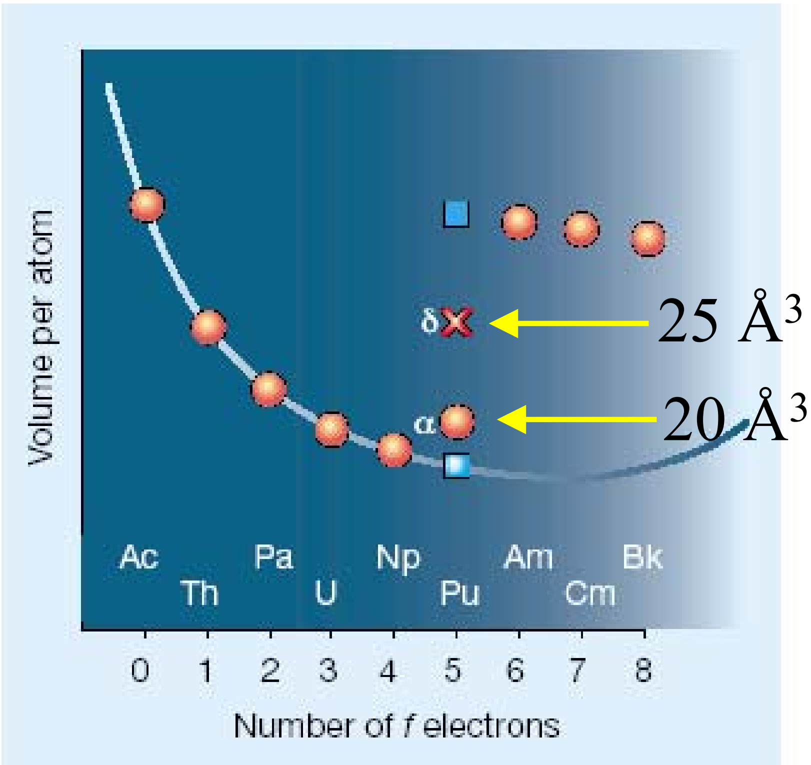
Structural and Electronic description of actinides requires determining the balance of electron correlation effects: Coulomb energy, electron exchange correlation, spin and orbital polarization, spin-orbit coupling and crystal field effects

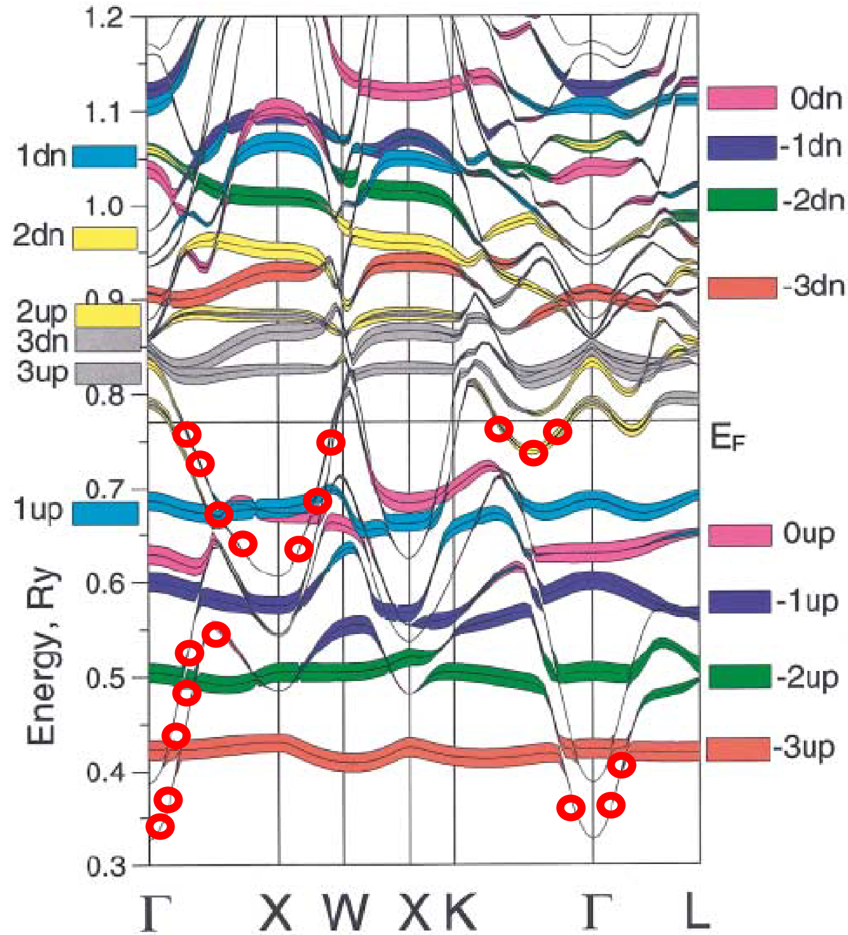
Coulomb energy proportional to 1/R
Electron exchange correlation proportional to $1/(R)^{2-3}$

Nanostructures provide the key advantage

It is plutonium's electronic structure that makes it the most complex and fascinating element – Los Alamos Science, 26, Vol I & II, 2000

The properties of the 5f electrons determine the behavior of actinides





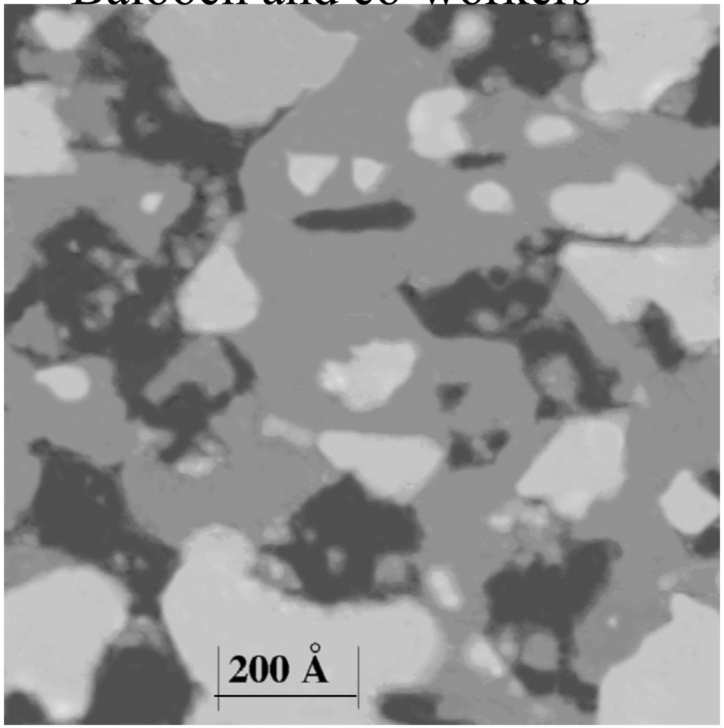
Albers, Nature 410, 759 (2001).

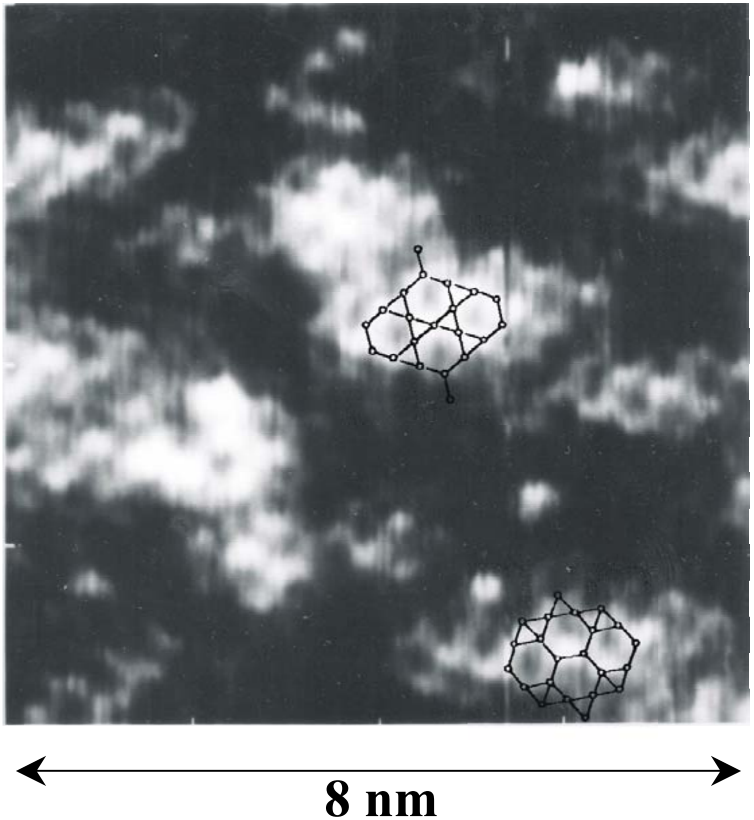
Savrasov and Kotliar, PRL 84 3670 (2000)

Three or four different electronic structure calculations with as many different predictions – **Experiments are needed**

Each atom is within a translation vector: crystalline 2D nanostructures

Balooch and co-workers





Scanning Tunneling Microscopy determines atomic structure of samples

2D Nanostructure: Crystalline β phase of Uranium grown on highly oriented pyrolytic graphite

Goal: **Provide clean nanoscale actinide material for experiments probing the structural and electronic properties of actinides materials**

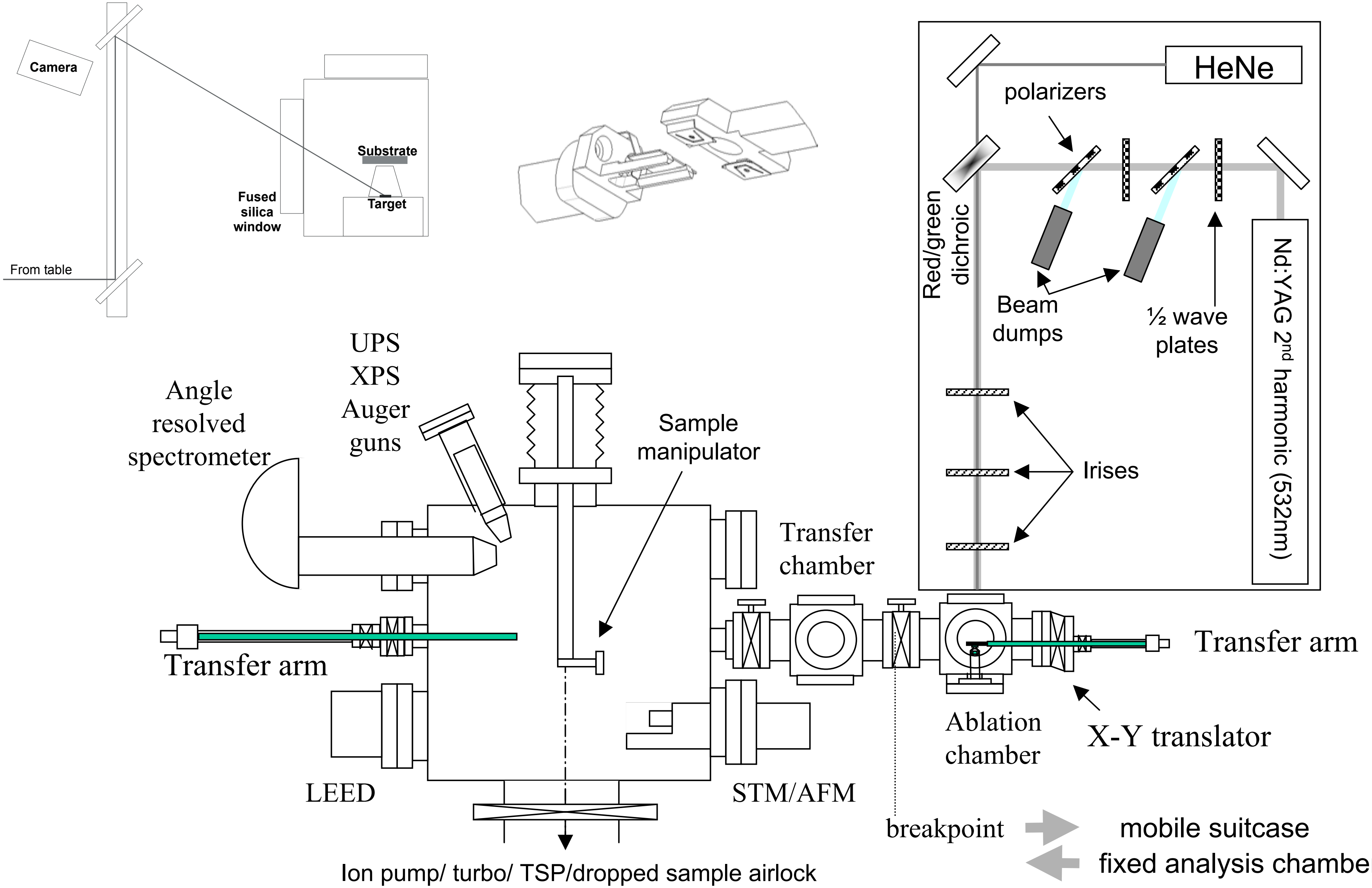
Requirements:

Conduct experiments on a small lab scale with off-the-shelf (and recycled) components

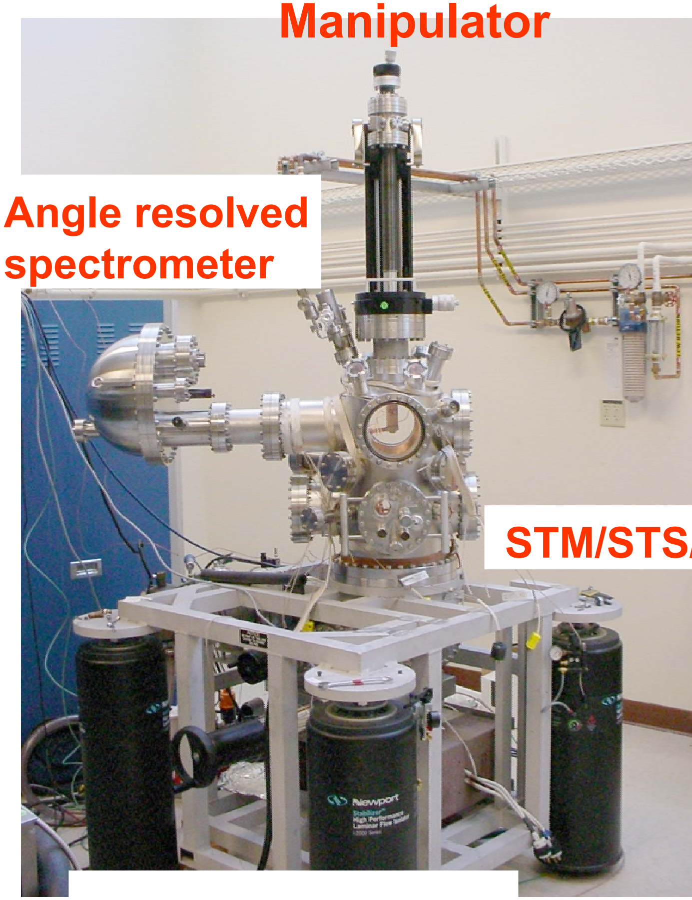
- Creation and analysis of ^{238}U and Pu samples via pulsed laser ablation.
  - -- ease of nanoparticle generation
  - -- control of growth properties
  - -- short pulse ablation can preserve stoichiometry
  - -- nanowires, thin films

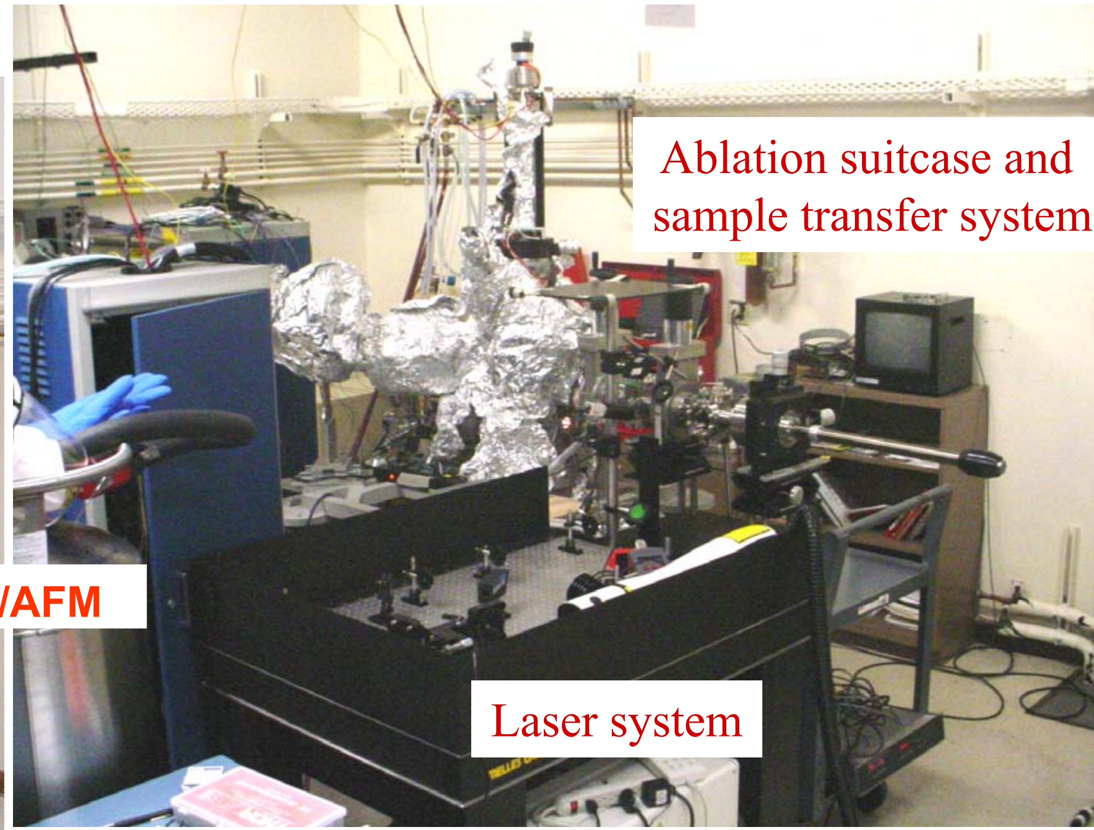
- Preservation of sample
  - -- oxidation (study and prevention)
  - -- sample transfer and retrieval

System layout

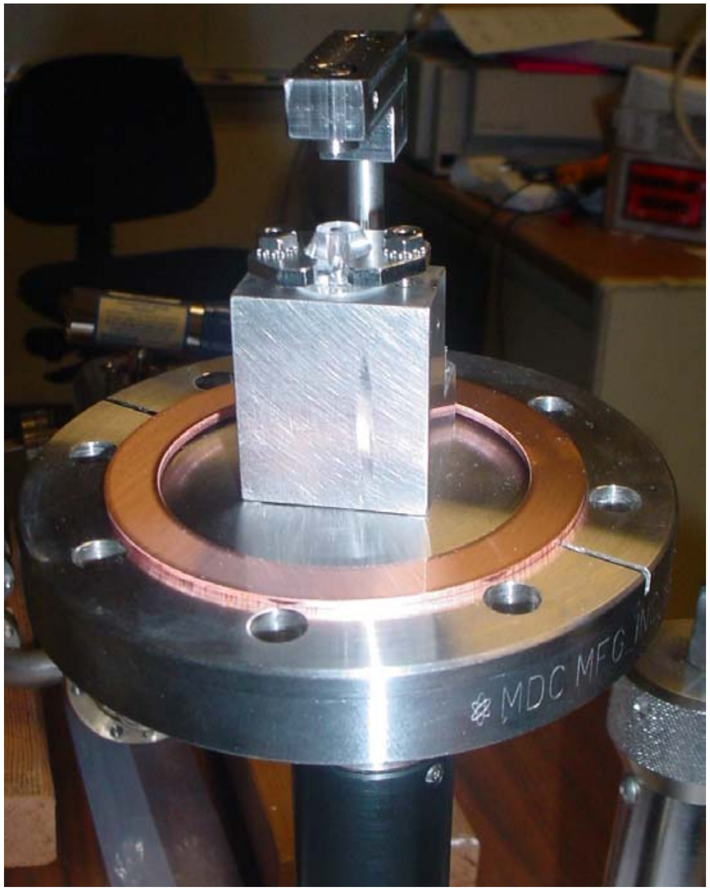


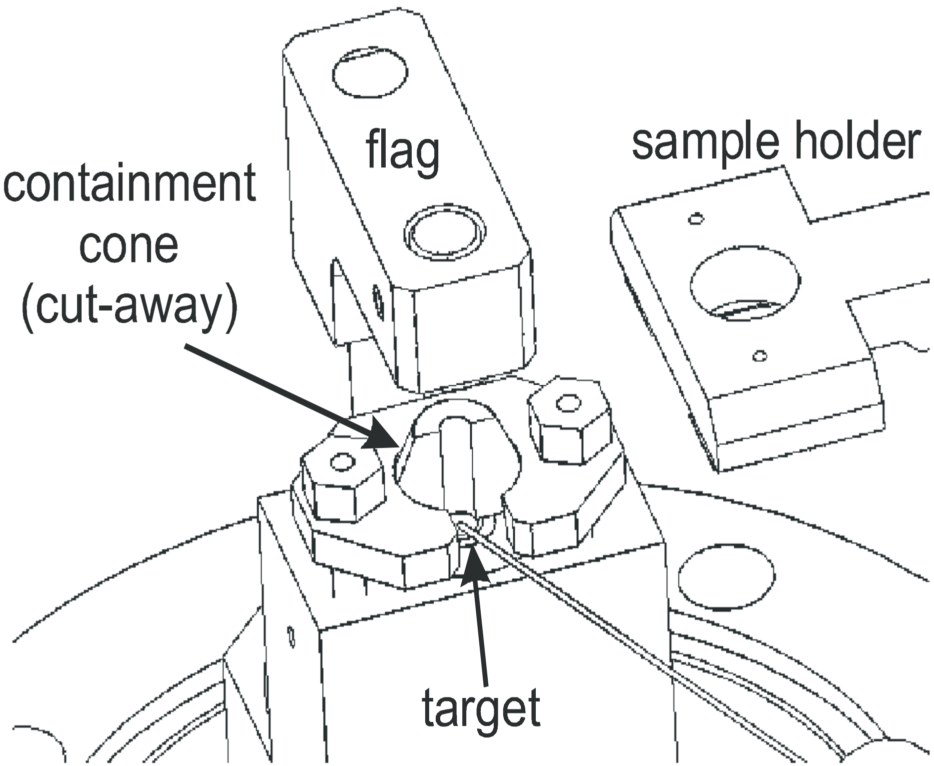
Actinide ablation system in 235/1210





Use of small, contained actinide samples circumvents need for bulk single crystal sample





Very small, contained ablation station for milligram Pu samples

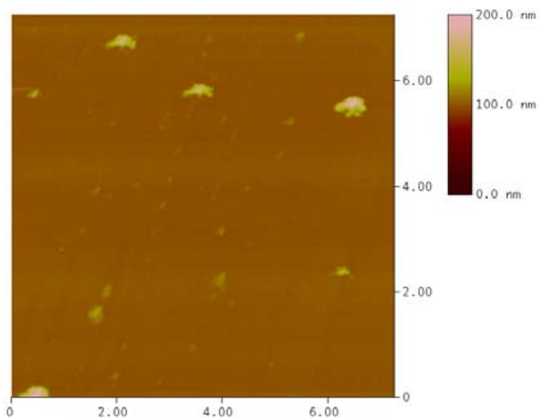
Morphology of uranium deposited via laser ablation

Uranium laser deposited on a Si substrate and transferred *in vacuo* to analysis chamber for photoemission spectrometry (PES). Following PES analysis, substrate was successfully returned to the ablation chamber and removed.

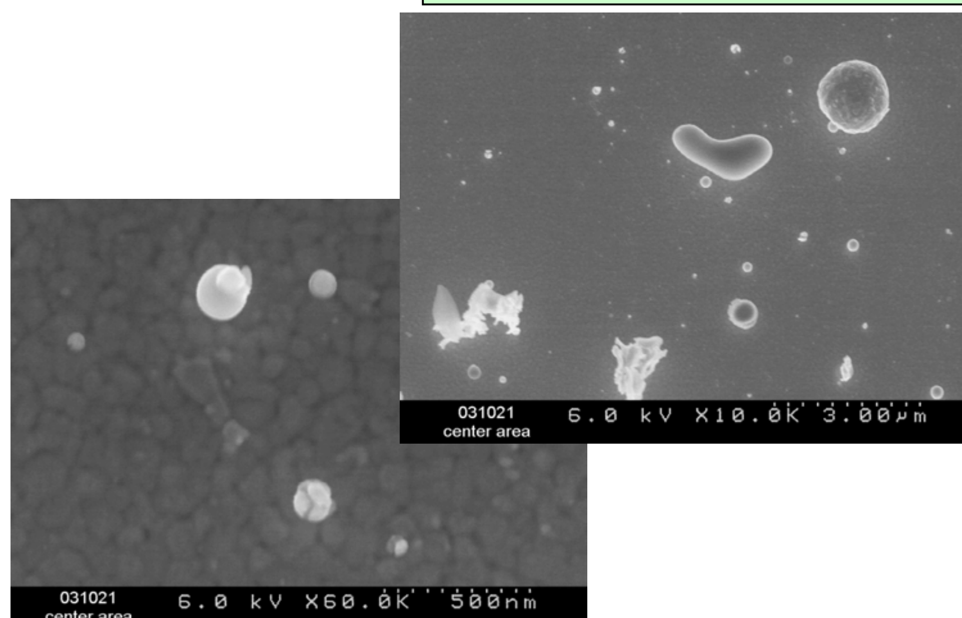
SEM

Various morphologies of uranium clusters ablated onto Au coated Si

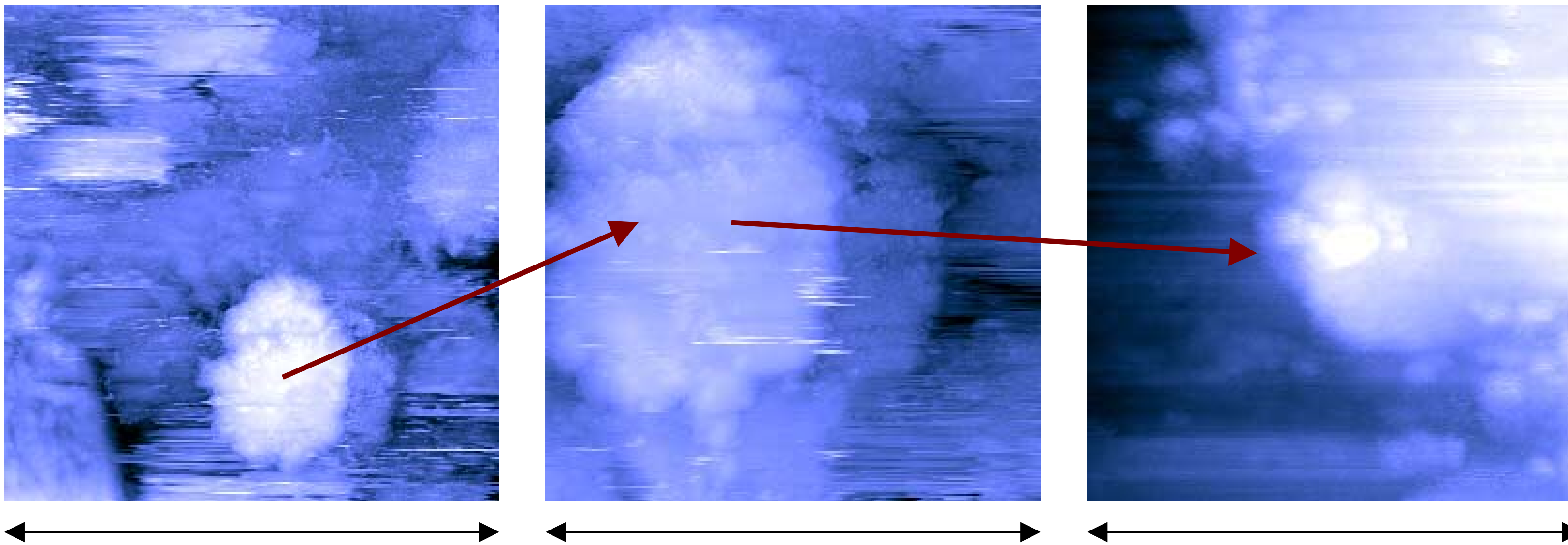
Scanned probe microscopy



100 - 200 nm uranium clusters laser ablated on SiO_2



In-situ STM of Uranium ablation products

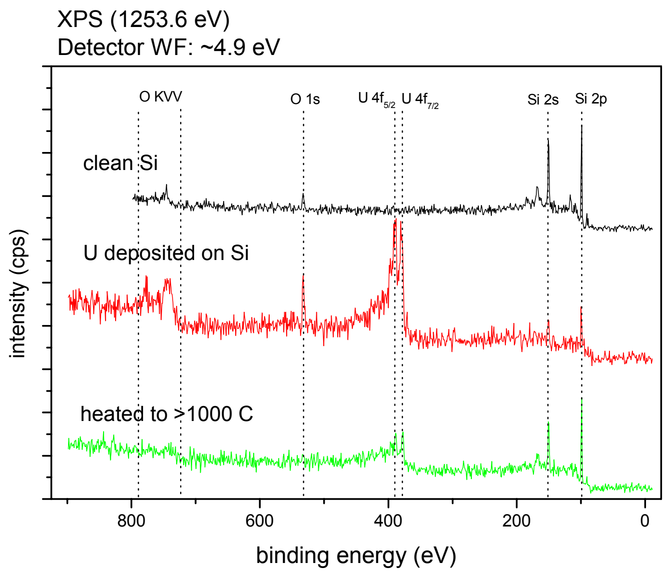


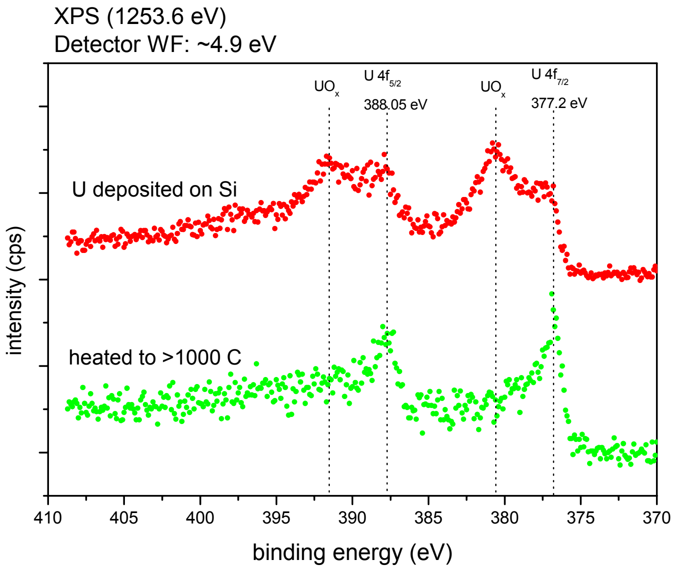
2 μm
white to black ~30 nm
0428008

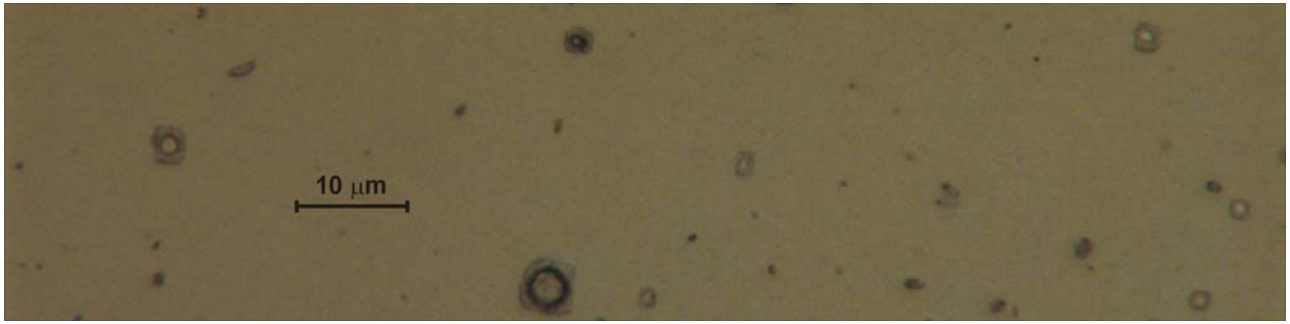
1 μm
white to black ~20 nm
042800a

100 nm
white to black ~8 nm
0428013

Annealing of samples

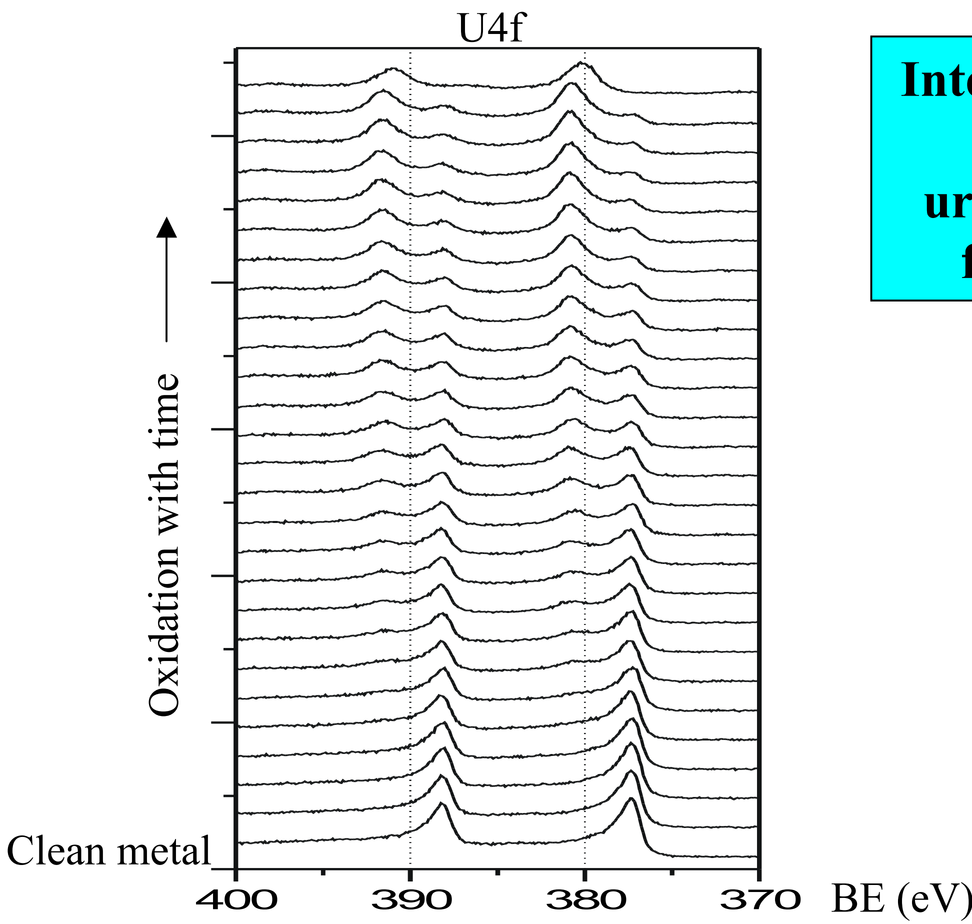




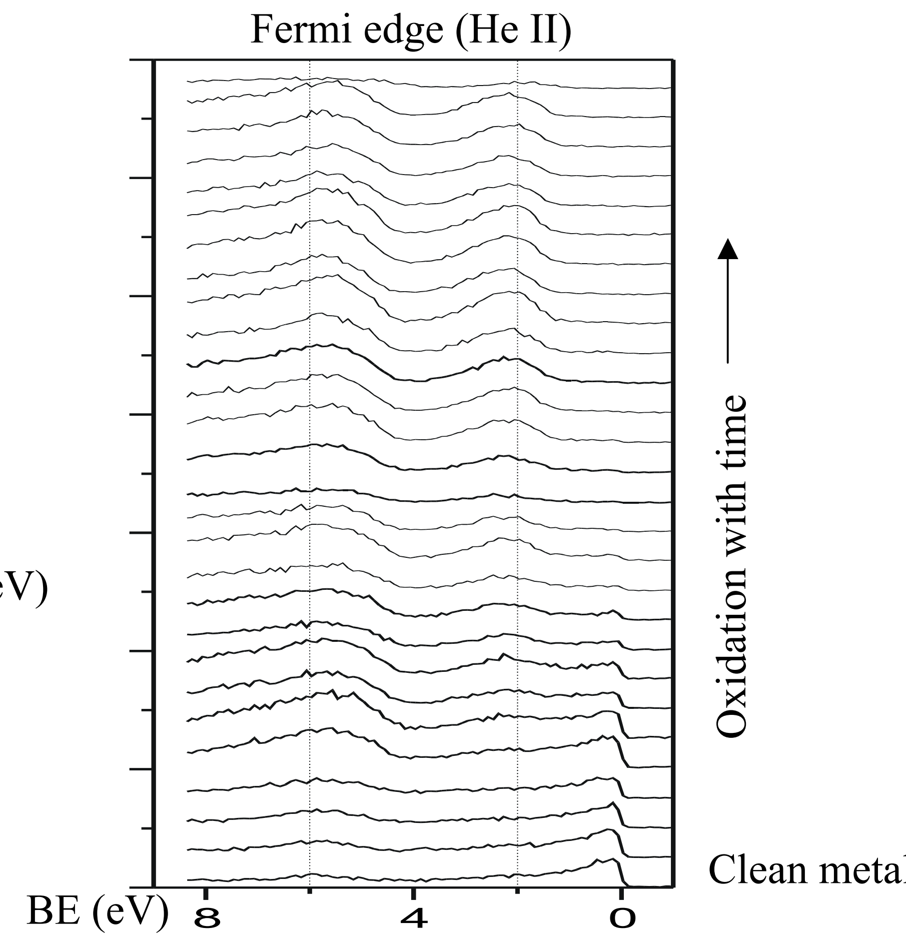


XPS shows reduced uranium signal following anneal. Optical microscopy gives evidence that of clean metal within an oxide shell. Anneal exceeded U melting point (~1100 C) and formed a silicide with the substrate (squarish crystallites). The oxide shell with a higher melting point (~2800 C) retains a spherical shape following the anneal.

Oxidation progression

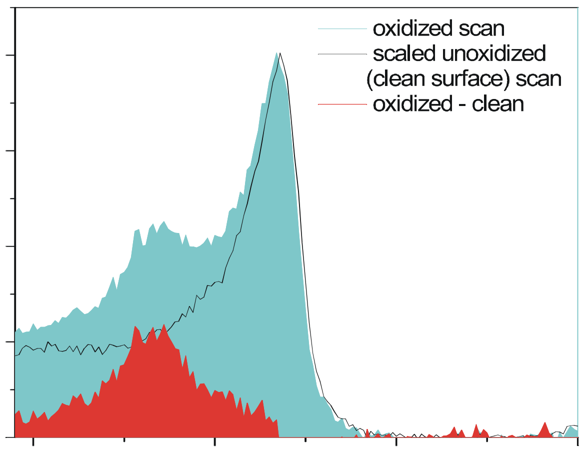


Intensity at ~6 eV is physisorbed oxygen (O2p) while intensity at ~3 eV is uranium 5f character shifted from the fermi edge by chemisorbed oxygen

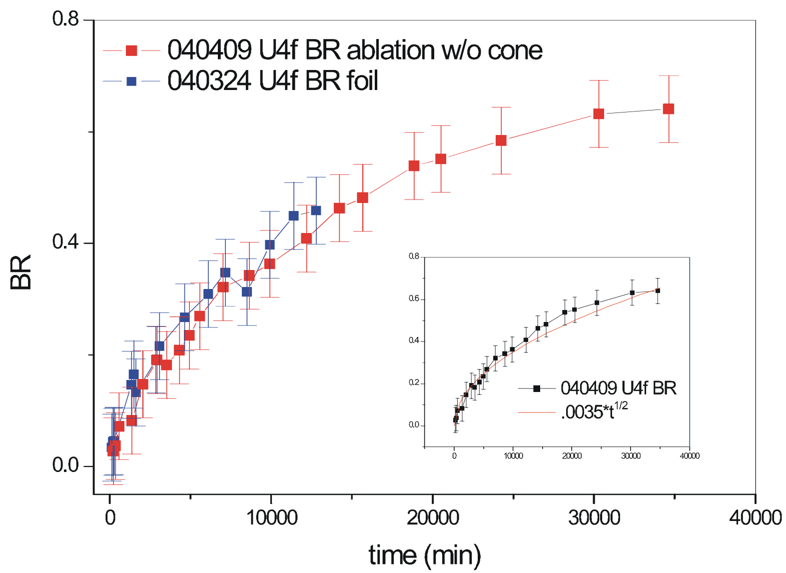


Oxide changes from UO_2 to UO_3 character with time at 1.5×10^{-10} Torr. Characteristic stoichiometry reverts to UO_2 on exposure to air

Oxidation progression (cont.)

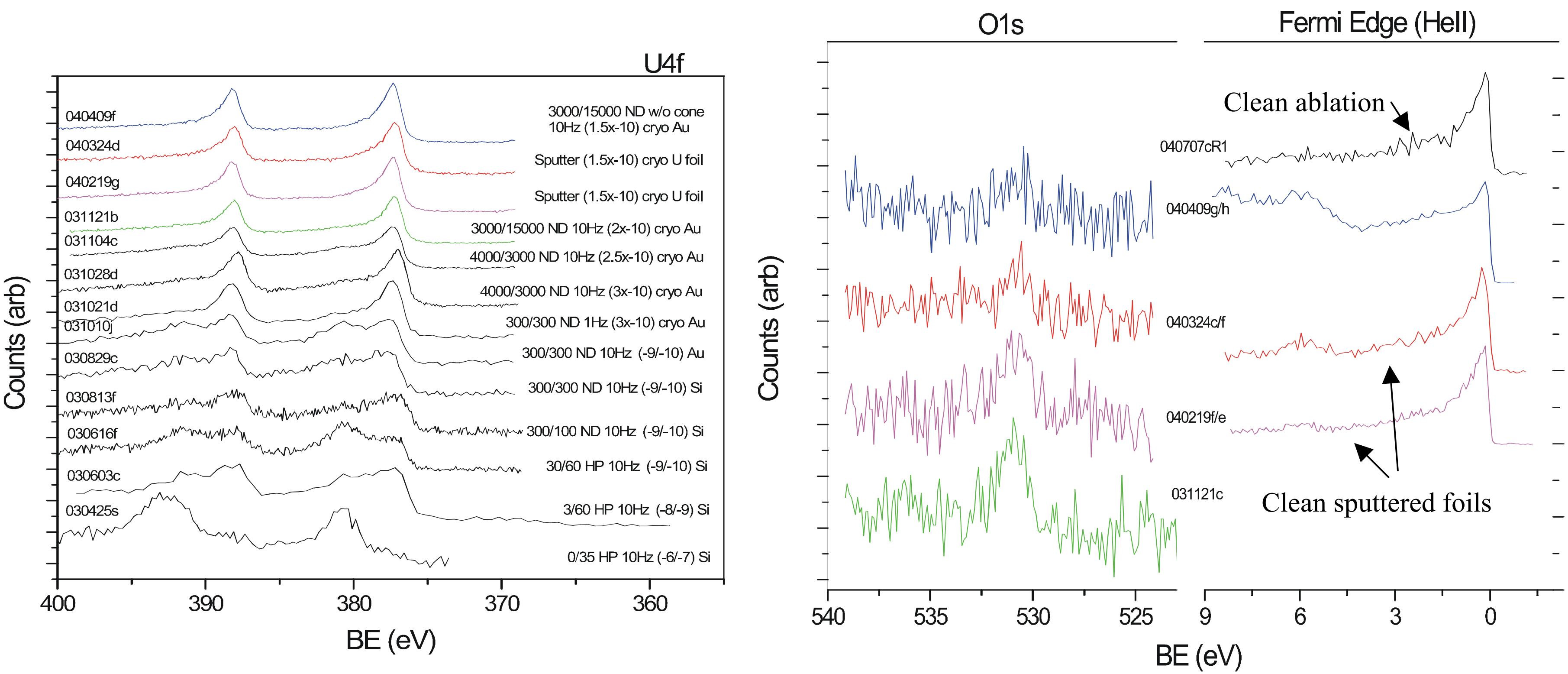


Oxidation has been quantified using branching ratios. An unoxidized scan is scaled so that its metallic intensity matches that of the oxidized scan and a difference is taken. The area of the difference is divided by the unoxidized area, giving a value between 0 (clean metal) and 1 (completely oxidized)



Branching ratios for both sputter cleaned foils and samples created via laser ablations appear to oxidize in the same manner. A $t^{1/2}$ dependence can be fit to the data, consistent with a diffusion mechanism

Clean uranium deposition requires tuning of system parameters



Minimizing background pressure as well as proper choice of ablation parameters (free/confined, power on target, number of shots) are vital.

Summary - Challenging project with high payoff

- We have demonstrated the potential of the technique
- Chief challenges are creating and characterizing clean ^{238}U and creating Pu samples.
- Future programmatic relevence:
  - Electronic structure of Pu-Ga alloys - sub-picosecond ablation should retain stoichiometric alloy composition.
  - Chemical studies – Oxidation and hydriding of Pu and alloys

Enabling small scale actinide experiments